

Superconductivity at 32 K in single crystal $\text{Rb}_{0.78}\text{Fe}_2\text{Se}_{1.78}$

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We successfully grew the high-quality single crystal of $\text{Rb}_{0.78}\text{Fe}_2\text{Se}_{1.78}$, which shows sharp superconducting transition in magnetic susceptibility and electrical resistivity. Resistivity measurements show the onset superconducting transition (T_c) at 32.1 K and zero resistivity at 30 K. From the low-temperature iso-magnetic-field magnetoresistance, large upper critical field $H_{c2}(0)$ has been estimated as high as 180 T for in-plane field and 59 T for out-of-plane field. The anisotropy $H_{c2}^b(0)/H_{c2}^c(0)$ is around 3.0, right lying between those observed in $\text{K}_x\text{Fe}_2\text{Se}_2$ and $\text{Cs}_x\text{Fe}_2\text{Se}_2$.

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The newly discovered iron-based superconductors have attracted worldwide attention in past three years[1–5] because of their high superconducting transition temperature (T_c as high as 55 K) and the fact that superconductivity emerges proximity to magnetically ordered state.[6, 7] The fact that superconductivity in iron-pnictide compounds is closely related to magnetic correlations inspires researchers tending to connect them with the high- T_c cuprates, in which superconductivity is realized by suppressing the antiferromagnetic Mott-insulating state, and attempting to understand the superconducting mechanism in the same theoretical scenario for the both families. Up to now, a variety of Fe-based superconductors, such as ZrCuSiAs -type LnFeAsO (Ln -1111, Ln is rare earth elements) [1–3], ThCr_2Si_2 -type AeFe_2As_2 (Ae -122, Ae is alkali earth elements) [4], Fe_2As -type AFeAs (A -111, A is Li or Na) [8–10] and anti- PbO -type $\text{Fe}(\text{Se}, \text{Te})$ (11)[12], have been discovered. Antiferromagnetic spin density wave instability usually exists in the parent compound of superconducting Ln -1111 and Ae -122, and even coexists with the superconductivity in slightly doping levels of Ln -1111, Ae -122 and A -111. While for 11 phase, the magnetism is quite complicated and its relationship to superconductivity remains more unrecognized.

All of the above mentioned Fe-base superconductors have a common structural feature with the edge-sharing FeAs_4 (FeSe_4) tetrahedra forming FeAs (FeSe) layers. The superconductivity in these compounds is thought to be intimately associated with the height of anion from Fe layer [11]. FeAs -based compounds usually possess cations or building block between the FeAs layers, while $\text{Fe}(\text{Se}, \text{Te})$ family has an extremely simple structure with only FeSe layers stacking along c -axis without other cations between them.[12] High pressure has been used to change the height of anion from Fe layer in $\text{Fe}(\text{Se}, \text{Te})$. Especially, T_c can reach 37 K (onset) under 4.5 GPa from

8 K in FeSe [13] with a pressure dependent ratio of T_c as large as $dT_c/dP \sim 9.1$ K/GPa, which is the highest pressure effect among all the Fe-base superconductors.[13] Ti has been attempted to intercalate into between the FeSe layers to change the local structure of FeSe family. However, an antiferromagnetic ordering forms at the temperature as high as 450 K,[14] and no superconductivity is observed in TiFe_2Se_2 . Very recently, the alkali atoms K and Cs are successfully intercalated into between the FeSe layers, and superconductivity has been enhanced from $T_c = 8$ K of pure FeSe to 30 K and 27 K (onset) without any external pressure.[15–18] It indicates that T_c in FeSe family can really be enhanced by intercalating cations into between the FeSe layers.

In this communication, we successfully grew the single crystals of a new superconductor $\text{Rb}_x\text{Fe}_2\text{Se}_2$ by using self-flux method. The crystals showed the onset T_c of 32.1 K and zero resistivity at about 30 K. Nearly 100% superconducting volume fraction was observed through the zero-field-cooling (ZFC) magnetic susceptibility measurements. Upper critical field $H_{c2}(0)$ was estimated from iso-magnetic-field magnetoresistance as high as 180 T with field applied in ab -plane and 59 T with field applied along c -axis.

Single crystals $\text{Rb}_x\text{Fe}_2\text{Se}_2$ were grown by self-flux method. Starting material FeSe was obtained by reacting Fe powder with Se powder with $\text{Fe}:\text{Se} = 1:1$ at 700°C for 4 hours. Rb pieces and FeSe powder were put into a small quartz tube with nominal composition of $\text{Rb}_{0.8}\text{Fe}_2\text{Se}_2$. Due to the high activity of Rb metal, the single wall quartz tube will be corrupted and broken during the growth procedure. Therefore, double wall quartz tube is used here. The small quartz tube was sealed under high vacuum, and then was put in a bigger quartz tube following by evacuating and being sealed. The mixture was heated to 980°C in 10 hours and kept for 4 hours, and then melt at 1080°C for 2 hours, and later slowly cooled down to 780°C with $6^\circ\text{C}/\text{hour}$. After that, the temperature was cooled down to room temperature by shutting down the furnace. The obtained single crystals show the flat shiny surface with dark black color. The crystals are easy to cleave and thin crystals with

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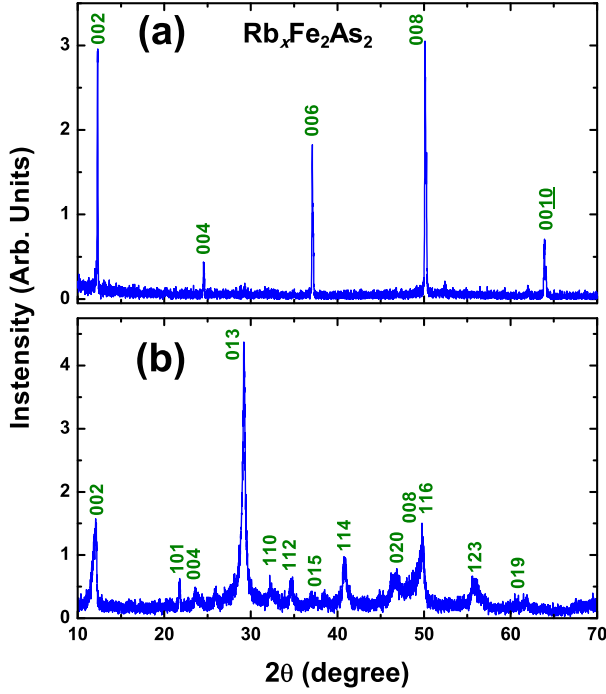


FIG. 1: (Color online) X-ray diffraction patterns for $\text{Rb}_x\text{Fe}_2\text{Se}_2$, (a): The single crystal X-ray diffraction pattern; (b): X-ray diffraction pattern of the powdered $\text{Rb}_x\text{Fe}_2\text{Se}_2$.

thickness less than $100\ \mu\text{m}$ can be easily obtained.

The single crystals were characterized by X-ray diffraction (XRD), Energy dispersive X-ray (EDX) spectroscopy, magnetic susceptibility, and electrical transport measurements. Powder XRD and single crystal XRD were performed on TTRAX3 theta/theta rotating anode X-ray Diffractometer (Japan) with $\text{Cu K}\alpha$ radiation and a fixed graphite monochromator. Magnetic susceptibility measurements were carried out using the *Quantum Design* MPMS-SQUID. The measurement of resistivity and magnetoresistance were done on the *Quantum Design* PPMS-9.

Figure 1 shows the X-ray single crystal diffraction (Fig. 1a) and powder XRD (Fig. 1b) after grounding the single crystals into powder. Only $(00l)$ reflections were recognized in Fig. 1a, indicating that the crystals of $\text{Rb}_x\text{Fe}_2\text{Se}_2$ were perfectly grown along c -axis. From the powder XRD patterns in Fig. 1b, the lattice constants were calculated based on the symmetry $I4/mmm$ with lattice parameters $a = 3.925\ \text{\AA}$ and $c = 14.5655\ \text{\AA}$. Lattice constants of a and c lie between those of $\text{K}_x\text{Fe}_2\text{Se}_2$ and $\text{Cs}_x\text{Fe}_2\text{Se}_2$, respectively. It is consistent with the expectation based on variation of the radius of the K, Rb, Cs ions (K 1.51\AA , Rb 1.63\AA , Cs 1.78\AA).^[19] The actual compositions of the crystals were determined by EDX using an average of different 4 points. It is found that the composition is homogeneous in the crystals. The actual composition is Rb: Fe: Se = 0.78: 2: 1.78, indicating the existence of deficiencies at K sites and Se sites. Such deficiency is similar to our previous report for $\text{K}_x\text{Fe}_2\text{Se}_2$

[18], but is sharply in contrast to other reports of both K and Fe deficiencies in $\text{K}_x\text{Fe}_2\text{Se}_2$ and $\text{Cs}_x\text{Fe}_2\text{Se}_2$.^[15–17]

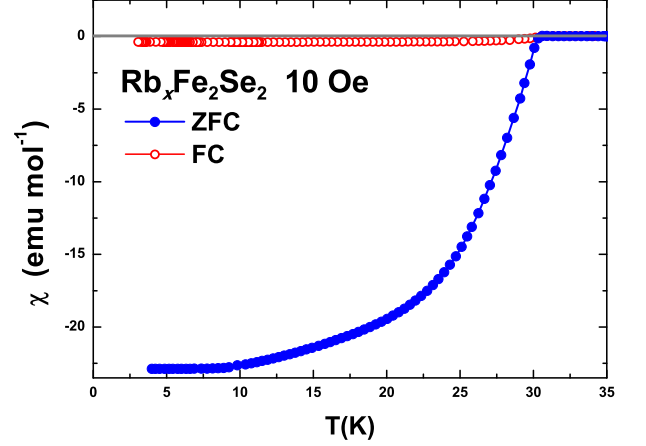


FIG. 2: (Color online) Temperature dependence of the Zero-field cooling and field cooling susceptibility taken at 10 Oe with the magnetic field parallel to the ab -plane for the single crystal $\text{Rb}_{0.78}\text{Fe}_2\text{Se}_{1.78}$.

Figure 2 shows magnetic susceptibility as a function of temperature below 35 K for single crystal $\text{Rb}_{0.78}\text{Fe}_2\text{Se}_{1.78}$ under a magnetic field of 10 Oe. The zero-field-cooling (ZFC) and field cooling (FC) susceptibilities show that the superconducting shield begins to emerge at about 30.6 K and then show a sharp transition. The ZFC magnetic susceptibility becomes saturation below 10 K, indicating high quality of single crystal. The superconducting volume fraction estimated from the ZFC magnetization at 4 K is 100%. All of these demonstrate a bulk superconductivity nature in $\text{Rb}_{0.78}\text{Fe}_2\text{Se}_{1.78}$ single crystals.

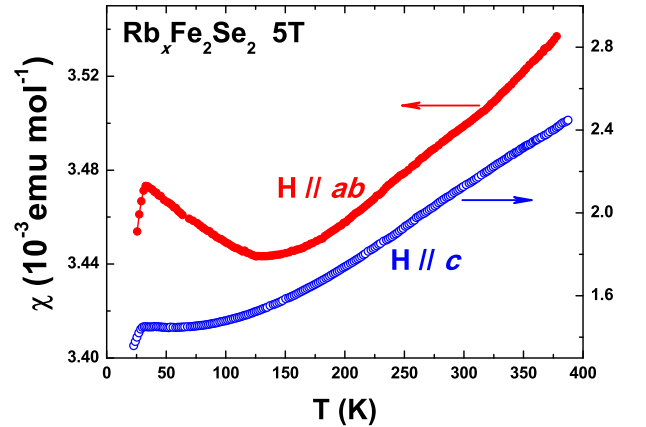


FIG. 3: (Color online) The magnetic susceptibility at 5 T for single crystal $\text{Rb}_{0.78}\text{Fe}_2\text{Se}_{1.78}$ with the magnetic field along and perpendicular to c -axis.

Figure 3 shows the magnetic susceptibility of $\text{Rb}_{0.78}\text{Fe}_2\text{Se}_{1.78}$ with the magnetic field of 5 T applied parallel and perpendicular to the c -axis from 10 K to 400

K. At low temperature, superconducting trace can still be found because of a drop of susceptibility. When magnetic field was applied along c -axis, the magnetic susceptibility gradually decreases with decreasing the temperature. The susceptibility shows a minimum at about 120 K with the magnetic field applied within ab -plane. Above 120 K, the susceptibility monotonically increases with increasing temperature; while gradually increases with decreasing temperature down to about 40 K just above superconducting transition temperature. Although the in-plane $\chi(T)$ shows a minimum 120 K above T_c , the magnitude of the susceptibility only changes by less than 2.5 % in the temperature range from 40 K to 400 K. Such behavior of susceptibility in $\text{Rb}_{0.78}\text{Fe}_2\text{Se}_{1.78}$ is exactly the same as that observed in $\text{Cs}_{0.86}\text{Fe}_{1.66}\text{Se}_2$. [18] Therefore, such peculiar behavior of susceptibility is common feature. The continuous decrease of susceptibility with decreasing the temperature suggests a strong antiferromagnetic spin fluctuation. Such spin fluctuation could be related to the superconductivity.

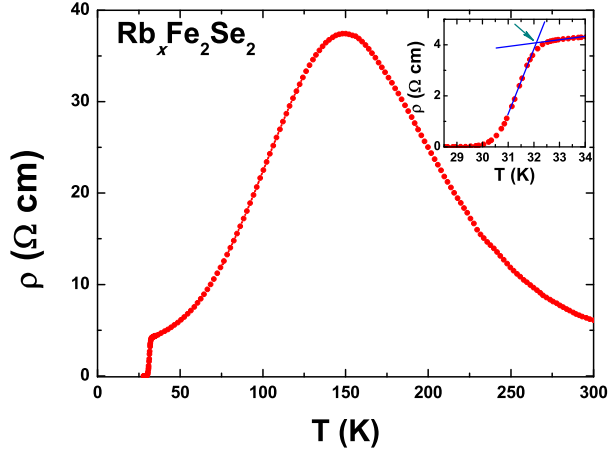


FIG. 4: (Color online) Temperature dependence of resistivity for single crystal $\text{Rb}_{0.78}\text{Fe}_2\text{Se}_{1.78}$. The inset is the zoom plot of resistivity around superconducting transition.

Figure 4 shows the in-plane resistivity as the function of temperature for the $\text{Rb}_{0.78}\text{Fe}_2\text{Se}_{1.78}$. The $\text{Rb}_{0.78}\text{Fe}_2\text{Se}_{1.78}$ shows the semiconductor-like behavior at the high temperature, and displays a maximum resistivity at about 150 K, and shows a metallic behavior below 150 K and a superconducting transition at about 32 K. Similar resistivity has been observed in $\text{K}_x\text{Fe}_2\text{Se}_2$. [15, 18] It seems that the resistivity behavior observed here is common feature. The temperature corresponding to the maximum resistivity in $\text{Rb}_{0.78}\text{Fe}_2\text{Se}_{1.78}$ is higher than that for $\text{K}_x\text{Fe}_2\text{Se}_2$ reported by Guo *et al.* (around 100 K) [15] and by Ying *et al.* (around 120 K) [18], while less than that reported by Mizuguchi *et al.* (~ 200 K). [16] The maximum resistivity in $\text{Rb}_{0.78}\text{Fe}_2\text{Se}_{1.78}$ crystal here (~ 37 Ω cm) is much larger than that of $\text{K}_x\text{Fe}_2\text{Se}_2$ in previous report (~ 3 Ω cm). [16] The temperature of the maximum resistivity strongly depends on the sample. The different temperature of the maximum resistivity could arise from

the vacancies at Fe or Se sites. The residual resistance ratio between 150 K and 33 K is as large as 9. With further decreasing the temperature, superconductivity emerges at about 32.1 K and resistivity reaches zero at around 30 K. These values are very close to those observed in $\text{K}_x\text{Fe}_2\text{Se}_2$. [15, 16] The resistivity of $\text{Rb}_{0.78}\text{Fe}_2\text{Se}_{1.78}$ crystal are 6 Ω cm at room temperature, which is much larger than those of FeSe single crystals [20] and the other iron-pnictide superconductors [21]. This may arise from the large disorder induced by deficiencies of Fe or Se. Occurrence of superconductivity in a system with so high resistivity demands further theoretical and experimental investigation.

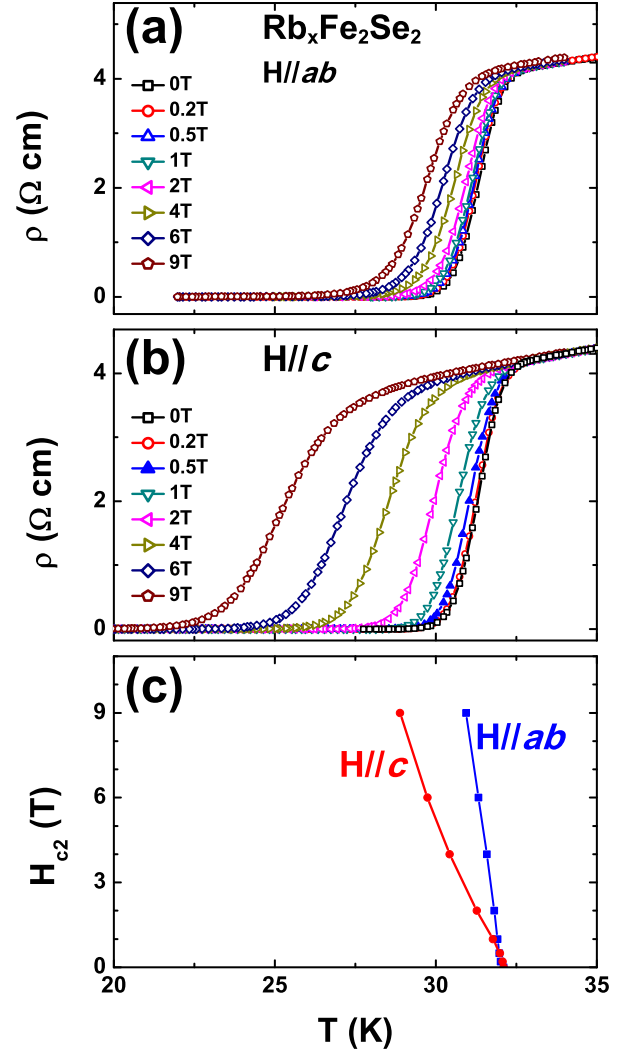


FIG. 5: (Color online) (a) and (b) show the temperature dependence of resistivity for $\text{Rb}_{0.78}\text{Fe}_2\text{Se}_{1.78}$ with the magnetic field parallel and perpendicular to the ab -plane, respectively; (c): The temperature dependence of upper critical field $H_{c2}(T)$ for $\text{Rb}_{0.78}\text{Fe}_2\text{Se}_{1.78}$.

Resistivity as a function of temperature under the magnetic field applied in ab -plane and along the c -axis is shown in Fig. 5a and 5b. The transition temperature of

superconductivity is suppressed gradually and the transition is broadened with increasing the magnetic field. Obvious difference for the effect of field along different direction on the superconductivity can be observed. In order to study this difference clearly, we defined the T_c as the temperature where the resistivity was 90% drop right above the superconducting transition. The anisotropic $H_{c2}(T)$ are shown in Fig. 5c for the two field directions, respectively. Within the weak-coupling BCS theory, the upper critical field at $T=0$ K can be determined by the Werthamer-Helfand-Hohenberg (WHH) equation[22] $H_{c2}(0) = 0.693[-(dH_{c2}/dT)]_{T_c} T_c$. From Fig. 5c, we can have $[-(dH_{c2}^{ab}/dT)]_{T_c} = 8.09$ T/K, $[-(dH_{c2}^c/dT)]_{T_c} = 2.66$ T/K and $T_c = 32.1$ K. Then the $H_{c2}(0)$ can be estimated to be 180 T and 59 T with the magnetic field applied in *ab*-plane and along the *c*-axis, respectively. These values are less than that in $K_x\text{Fe}_2\text{Se}_2$ [16, 18], while larger than that in CsFe_2Se_2 . [18] The anisotropy $H_{c2}^{ab}(0)/H_{c2}^c(0)$ is about 3.0 and this value just lies right between $K_x\text{Fe}_2\text{Se}_2$ and $\text{Cs}_x\text{Fe}_2\text{Se}_2$. This anisotropy value is larger than 1.70~1.86 in $\text{Ba}_{0.60}\text{K}_{0.40}\text{Fe}_2\text{As}_2$ [23], while less than 4~6 in F-doped NdFeAsO [24].

We have systematically grown the single crystals $A_x\text{Fe}_2\text{Se}_2$ ($A = \text{K}, \text{Cs}$ and Rb). It is found that there exist some common features in resistivity and magnetic properties for these crystals. A maximum resistivity as shown in Fig. 4 is widely observed in $K_x\text{Fe}_2\text{As}_2$ [15, 16, 18] and $\text{Rb}_x\text{Fe}_2\text{As}_2$. Another common feature is that peculiar behavior of normal state susceptibility as shown in Fig.3 is widely observed in $\text{Cs}_x\text{Fe}_2\text{As}_2$ [18] and $\text{Rb}_x\text{Fe}_2\text{As}_2$. It is found based on the observation in Fig. 3 and 4 that the maximum resistivity nearly coincides with the minimum susceptibility

with magnetic field applied within *ab*-plane. It suggests that there exists a correlation between the maximum resistivity and the minimum in-plane susceptibility. It should be addressed that the deficiency of Fe and Se is related to the ionic radius of alkali metals K, Rb and Cs. The actual compositions of superconducting crystals are $\text{K}_{0.86}\text{Fe}_2\text{Se}_{1.82}$ [18], $\text{Rb}_{0.78}\text{Fe}_2\text{Se}_{1.78}$ and $\text{Cs}_{0.86}\text{Fe}_{1.66}\text{Se}_2$. It indicates that the vacancy in conducting FeSe layers changes from Se site to Fe site with increasing the ionic radius of alkali metals from K to Cs. It is found that normal state resistivity and susceptibility strongly depend on the vacancy in conducting FeSe layers. Further study on the origin of the deficiency of Fe and Se should be required to understand the normal state behavior, even the superconductivity of $A_x\text{Fe}_2\text{Se}_2$ materials.

In conclusion, we successfully grew a new superconductor $\text{Rb}_{0.78}\text{Fe}_2\text{Se}_{1.78}$ single crystals. T_c^{onset} is 32.1 K determined by resistivity measurement and zero resistivity is reached at 30 K. The ZFC dc magnetic susceptibility indicates that the crystal is fully diamagnetic. The large $H_{c2}(0)$ is observed, being similar to that in other the iron-pnictide superconductors[25]. The anisotropy $H_{c2}^{ab}(0)/H_{c2}^c(0)$ is 3.0, right lying between those of $K_x\text{Fe}_2\text{Se}_2$ and $\text{Cs}_x\text{Fe}_2\text{Se}_2$. A common peculiar susceptibility at the normal state is observed in $\text{Rb}_{0.78}\text{Fe}_2\text{Se}_{1.78}$.

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- [1] Yoichi Kamihara, Takumi Watanabe, Masahiro Hirano and Hideo Hosono, *J. Am. Chem. Soc.* **130**, 3296 (2008).
 - [2] X. H. Chen, T. Wu, G. Wu, R. H. Liu, H. Chen and D. F. Fang, *Nature* **453**, 761(2008).
 - [3] Z. A. Ren, W. Lu, J. Yang, W. Yi, X. L. Shen, Z. C. Li, G. C. Che, X. L. Dong, L. L. Sun, F. Zhou and Z. X. Zhao, *Chin. Phys. Lett.* **25**, 2215(2008).
 - [4] M. Rotter, M. Tegel, D. Johrendt, *Phys. Rev. Lett.* **101**, 107006(2008).
 - [5] R. H. Liu, G. Wu, T. Wu, D. F. Fang, H. Chen, S. Y. Li, K. Liu, Y. L. Xie, X. F. Wang, R. L. Yang, L. Ding, C. He, D. L. Feng and X. H. Chen, *Phys. Rev. Lett.* **101**, 087001 (2008).
 - [6] H. Chen, Y. Ren, Y. Qiu, Wei Bao, R. H. Liu, G. Wu, T. Wu, Y. L. Xie, X. F. Wang, Q. Huang and X. H. Chen, *Europhys. Lett.* **85**, 17006(2009).
 - [7] Clarina de la Cruz, Q. Huang, J. W. Lynn, Jiying Li, W. Ratcliff II, J. L. Zarestky, H. A. Mook, G. F. Chen, J. L. Luo, N. L. Wang and Pengcheng Dai, *Nature* **453** 899 (2008).
 - [8] X. C. Wang, Q. Q. Liu, Y. X. Lv, W. B. Gao, L. X. Yang, R. C. Yu, F. Y. Li, and C. Q. Jin, *Solid State Commun.* **148**, 538 (2008).
 - [9] J. H. Tapp, Z. Tang, B. Lv, K. Sasmal, B. Lorenz, Paul C.W. Chu, and A. M. Guloy, *Phys. Rev. B* **78**, 060505(R) (2008).
 - [10] D. R. Parker, M. J. Pitcher, P. J. Baker, I. Franke, T. Lancaster, S. J. Blundell, and S. J. Clarke, *Chem. Commun. (Cambridge)*, 2009, 2189.
 - [11] Y. Mizuguchi, Y. Hara, K. Deguchi, S. Tsuda, T. Yamaguchi, K. Takeda, H. Kotegawa, H. Tou and Y. Takano, *Supercond. Sci. Technol.* **23** 054013(2010).
 - [12] F. C. Hsu, J. Y. Luo, K. W. The, T. K. Chen, T. W. Huang, P. M. Wu, Y. C. Lee, Y. L. Huang, Y. Y. Chu, D. C. Yan and M. K. Wu, *Proc. Nat. Acad. Sci.* **105**, 14262 (2008).
 - [13] S. Medvedev, T. M. McQueen, I. Trojan, T. Palasyuk, M. I. Erements, R. J. Cava, S. Naghavi, F. Casper, V. Ksenofontov, G. Wortmann and C. Felser, *Nature Mater.* **8** 630(2009).
 - [14] J. J. Ying, A. F. Wang, Z. J. Xiang, X. G. Luo, R. H. Liu, X. F. Wang, Y. J. Yan, M. Zhang, G. J. Ye, P. Cheng and X. H. Chen, *arXiv*: 1012.2929.
 - [15] J. Guo, S. Jin, G. Wang, S. Wang, K. Zhu, T. Zhou, M. He and X. Chen, *Phys. Rev. B* **82**, 180520 (2010).
 - [16] Yoshikazu Mizuguchi, Hiroyuki Takeya, Yasuna

- Kawasaki, Toshinori Ozaki, Shunsuke Tsuda, Takahide Yamaguchi and Yoshihiko Takano, arXiv:1012.4950 (unpublished).
- [17] A. Krzton-Maziopa, Z. Shermadini, E. Pomjakushina, V. Pomjakushin, M. Bendele, A. Amato, R. Khasanov, H. Luetkens and K. Conder, arXiv:1012.3637.
 - [18] J. J. Ying, X. F. Wang, X. G. Luo, A. F. Wang, M. Zhang, Y. J. Yan, Z. J. Xiang, R. H. Liu, P. Cheng, G. J. Ye and X. H. Chen, arXiv: 0169761
 - [19] R. D. Shannon, *Acta. Cryst. A* **32**, 751 (1976).
 - [20] D. Braithwaite, B. Salce, G. Lapertot, F. Bourdarot, C. Marin, D. Aoki, and M. Hanfland, *J. Phys.: Condens. Matter* **21** 232202 (2009).
 - [21] X. F. Wang, T. Wu, G. Wu, R. H. Liu, H. Chen, Y. L. Xie, X. H. Chen, *New J. Phys.* **11**, 045003 (2009).
 - [22] N. R. Werthamer, E. Helfand, and P. C. Hohenberg, *Phys. Rev.* **147**, 295 (1966).
 - [23] ZhaoSheng Wang, Hui-Qian Luo, Cong Ren and Hai-hu Wen, *Phy. Rev. B* **78**, 140501(R) (2008).
 - [24] Ying Jia, Peng Cheng, Lei Fang, Huiqian Luo, Huan Yang, Cong Ren, Lei Shan, Changzhi Gu, and Hai-Hu Wen, *Appl. Phys. Lett.* **93**, 032503 (2008).
 - [25] H. Q. Yuan, J. Singleton, F. F. Balakirev, S. A. Baily, G. F. Chen, J. L. Luo and N. L. Wang, *Nature* **457**, 565 (2009).